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(54) Title: HOCKEY STICK BLADE HAVING AN ABRASION RESISTANT COATING AND PROCESS FOR COATING SAID BLADE

(57) Abstract

The invention relates to a hockey stick blade having an abrasion resistant coating, to a hockey stick comprising such a blade and to a process for coating a hockey stick blade. The coating is made from polyurethane or a mixture of polyurethane and polyurea and has a durometer hardness of at least about 70A. In a preferred embodiment, the coating may be made by mixing a urethane prepolymer having isocyanate terminal groups with an amine component. The coating of the present invention is particularly useful on harsh surfaces such as roller hockey surfaces and allows a player to use a stick that possesses better feel while reducing friction and abrasion.

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TITLE: HOCKEY STICK BLADE HAVING AN ABRASION RESISTANT COATING AND PROCESS FOR COATING SAID BLADE

FIELD OF THE INVENTION

The present invention relates to the field of hockey sticks and particularly to a hockey stick blade having improved wear properties. More particularly, the invention relates to a hockey stick blade comprising an abrasion resistant coating.

BACKGROUND TO THE INVENTION

The recent rise in popularity of in-line roller skates for use in leisure sport has also found it way into the field of hockey, the sport being commonly referred to as "in-line hockey" or "roller hockey". Traditionally, hockey has been practised on an ice rink whose surface is smooth and very slippery. Unlike ice hockey however, the surface on which roller hockey is played is somewhat harsh and as a result, increases the abrasion and the wear of the blade of a hockey stick. The harshness of the surface also means that the blade should exert as little friction as possible so as to be able to "glide" more easily on the surface of play.

In order to overcome the problems associated with abrasion, hockey stick manufacturers have suggested using stick blades made from various synthetic materials such as acrylonitrile-butadiene-styrene polymers (ABS) which are more resistant to wear. These hockey sticks have not however provided satisfactory results. Since traditional hockey sticks are constructed of wood, either alone or in combination with various composites such as fibreglass, carbon fibres or the like, they possess a certain feel to which hockey players have become accustomed. This "wood-like" feel is not present in the

conventional ABS roller hockey stick. Thus, the player is left with two unsatisfactory choices; either to play with a conventional hockey stick which provides the appropriate feel but that is subject to accelerated wear of the blade or to play with a synthetic stick that is more resistant to abrasion but that does not possess the appropriate feel.

In order to improve the wear properties of the blade, some manufacturers have also suggested using prepolymerized resins, such as phenoxy resins, dissolved in a volatile solvent such as a ketone. Other manufacturers have suggested using elastomeric coatings. These coatings have however been unsatisfactory for various reasons including, among others, their incapacity to resist wear over a relatively long period of time and their tendency to become brittle, i.e. their incapacity to deform before breaking when provided with a hardness that is high enough to adequately reduce friction. Yet another major disadvantage of using such coatings is the necessity to use organic solvents which are rather harmful to the environment and which have other associated disadvantages.

There is thus a need for a hockey stick blade comprising an abrasion resistant coating that will exhibit a level of hardness high enough to resist wear and adequately reduce friction without having a tendency to become brittle.

OBJECTS AND STATEMENT OF THE INVENTION

It is therefore an object of the present invention to provide a hockey stick blade which is more abrasion resistant than a conventional hockey stick blade.

A further object of the invention is to provide a hockey stick blade comprising an abrasion resistant coating having a hardness sufficient to prevent accelerated wear while adequately reducing friction.

As embodied and broadly described herein, the invention provides a hockey stick blade having a lower edge for contacting a surface of play, at least a portion of the lower edge bearing an abrasion resistant coating comprising polyurethane, the coating having a durometer hardness of at least about 70A.

In a preferred embodiment, the coating comprises polyurethane and polyurea, and most preferably, the coating is made by mixing a urethane prepolymer having isocyanate terminal groups with an amine component.

In one embodiment, the urethane prepolymer is made by reacting a mixture of toluene-2,4-diisocyanate and toluene-2,6-diisocyanate with an α,ω-glycol having between 2 and 6 carbon atoms, mixtures thereof or a low molecular weight polymer thereof and the amine component is a diamine which is mixed with an α,ω-glycol having between 2 and 6 carbon atoms or mixtures thereof.

Most preferably, the urethane prepolymer is made by reacting a mixture of toluene-2,4-diisocyanate and toluene-2,6-diisocyanate with an α-hydro-ω-hydroxypoly (oxy-1,4-butanediyl) and the amine component is a mixture of 4,4'-methylene dianiline with an α-hydro-ω-hydroxypoly [oxy(methyl-1,2-ethanediyl)].

As embodied and broadly described herein, the invention also provides a hockey stick blade having a lower edge for contacting a surface of play, at least a portion of the lower edge bearing an abrasion resistant coating having a durometer hardness of at least about 70A, the coating being made by

mixing a urethane prepolymer with an amine component, the urethane prepolymer being made by reacting an approximately 80:20 mixture of toluene-2,4-diisocyanate and toluene-2,6-diisocyanate with an approximately 90:10 mixture of two α-hydro-ω-hydroxypoly (oxy-1,4-butanediyls) having molecular weights of about 1000 and about 2000, respectively, the amine component being a mixture of 4,4'-methylene dianiline with an approximately 75:25 mixture of two α-hydro-ω-hydroxypoly [oxy(methyl-1,2-ethanediyls)] having molecular weights of about 1000 and about 500, respectively.

In another embodiment, the coating is made by mixing a diisocyanate with an amine mixture comprising an amine component, an α,ω-glycol having between 2 and 6 carbon atoms, mixtures thereof or a low molecular weight polymer thereof. Preferably, the diisocyanate is diphenylmethane diisocyanate and the amine mixture comprises an α-hydro-ω-hydroxypoly (oxy-1,4-butanediyl), 4,4'-methylene dianiline and an α-hydro-ω-hydroxypoly [oxy(methyl-1,2-ethanediyl)].

In a preferred embodiment, the coating has a durometer hardness between about 70A and 75D.

Preferably, the coating is between 20 to 30 mils thick and may comprise a pigment.

In another aspect, the invention also provides a hockey stick comprising a blade coated in accordance with the teachings of the present invention.

As embodied and broadly described herein, the invention also provides a process for coating a hockey stick blade, the process comprising the step of applying to a blade a coating comprising polyurethane and having a

durometer hardness of at least 70A, the process being carried out in the absence of or substantially in the absence of solvent.

In a preferred embodiment, the process comprises the steps of:

a) reacting a mixture of toluene-2,4-diisocyanate and toluene-2,6-diisocyanate with an α,ω-glycol having between 2 and 6 carbon atoms, mixtures thereof or a low molecular weight polymer thereof to form a urethane prepolymer;

b) mixing a diamine with an α,ω-glycol having between 2 and 6 carbon atoms or mixtures thereof to provide an amine component;

c) mixing the urethane prepolymer and the amine component to form a coating composition; and

d) applying the composition to the blade.

In a preferred embodiment, the urethane prepolymer and the amine component are heated to a temperature of about 70°C ± 10°C before being admixed and applied to the blade.

Most preferably, the urethane prepolymer of step a) is made by reacting a mixture of toluene-2,4-diisocyanate and toluene-2,6-diisocyanate with an α-hydro-ω-hydroxypoly (oxy-1,4-butanediyl) and the amine component of step b) is a mixture of 4,4'-methylene dianiline with an α-hydro-ω-hydroxypoly [oxy(methyl-1,2-ethanediyl)]. Preferably, the process is carried out in the absence of or substantially in the absence of solvent.

The blade coated in accordance with the invention has the advantage of preventing accelerated wear due to harsher playing surfaces while reducing friction. The inventor has also discovered that the coating of the present invention is advantageous when used on traditional ice hockey rinks. Indeed, although ice surfaces are not as harsh as roller hockey surfaces, ice hockey stick blades are nonetheless subjected to abrasion. This condition

should be avoided since as a result of the abrasion, water tends to penetrate inside the blade and reach the fibreglass, if any, thereby contributing to the delamination of the components of the stick which, over time, induces structural failure to the stick. This problem may be avoided by providing an ice hockey stick blade with the coating of the present invention.

Other objects and features of the invention will become apparent by reference to the following description of a preferred embodiment.

DESCRIPTION OF A PREFERRED EMBODIMENT

The inventors have discovered that the objects of the present invention could be achieved by providing a coating having a durometer hardness of at least about 70A when measured in accordance with the ASTM D-2240 test. More precisely, the inventors have realized that a suitable coating having such properties may be obtained by using a composition comprising polyurethane or a mixture of polyurethane and polyurea.

In accordance with a preferred embodiment of the invention, a coating is provided on the lower edge of the blade of a hockey stick. For the purpose of this specification, the expression "lower edge" is intended to cover the portion of the blade that is in contact with a surface of play. The coating can be applied on the entire edge or simply on the area that contacts the surface of play such as, for example, the heel portion. Similarly, the blade could be provided with a coating that is thicker at the heel portion and thinner at the front portion. In yet another embodiment, the coating could be applied on the entire blade.

A coating according to a first embodiment of the invention may consist of a polyurethane made by reacting an isocyanate and a polyol.

The isocyanate may be a diisocyanate or a triisocyanate. Suitable diisocyanates for use in preparing the coating of the present invention comprise preferably a mixture of toluene-2,4-diisocyanate and toluene-2,6-diisocyanate and their derivatives. A preferred diisocyanate is an approximately 80:20 mixture of toluene-2,4-diisocyanate and toluene-2,6-diisocyanate. Such a mixture is commercially available and is sold under the trademark MONDUR TD-80 (Product of Bayer). Other suitable diisocyanate include diphenylmethane diisocyanate, naphthylene diisocyanate, α,ω-alkylene diisocyanates such as hexamethylene diisocyanate and its derivatives an homologues. Suitable triisocyanates include triphenylmethane-*pp'p"*-triyl triisocyanate.

Suitable polyhydroxy compounds (polyols) that react with the diisocyanates or triisocyanates include diols or triols. Amongst the suitable diols are α,ω-glycols having between 2 and 6 carbon atoms or mixtures thereof, the glycols being preferably straight chain. A most preferred diol is α-hydro-ω-hydroxypoly (oxy-1,4-butanediyl) having a molecular weight of about 1000 or a molecular weight of about 2000 or blends thereof. Such products are commercially available under the trademarks TERATHANE 1000 and 2000 (products of DuPont). The use of triols is also contemplated. Amongst the suitable triols are polyoxypropylene triols. However the use of triols may make it more difficult to control the properties of the coating composition.

The coating of the present invention may also comprise some of the additives that are commonly found in such compositions. Amongst the additives are pigments used to add colour to the coating. These pigments may be carbon black, titanium dioxide or iron oxide and are usually added in an amount not exceeding 1%. The composition may also comprise a slip agent compatible therewith to provide good slip properties to the coating. Examples of slip agents include fatty acids derivatives such as oleamide. When present, these agents are added in an amount not exceeding 0.1%. To prevent

photochemical degradation and accelerated oxidation of the coating as a result of exposure to UV radiation, there may also be provided a UV stabilizer. Both the choice and the type of UV stabilizer may be determined by the person skilled in the art. Other additives such as fillers, antioxidants, thickeners or emulsifiers may also be included in the composition.

The coating should be within the specified range since a coating having a durometer hardness below about 70A may be too soft and may not allow the player to benefit from the reduced friction. On the other hand, the inventor has realized that a coating having a durometer hardness above about 75D may have a tendency to become brittle and as a result, the durometer hardness of the coating should not exceed 75D. However, the person skilled in the art will realize that the maximum value for the hardness may only depend on the desired applications and this limitation should not be interpreted in a limiting manner.

The person skilled in the art will realize that it is possible to adjust the hardness of the coating by using various additives or by modifying the type of isocyanate or polyol so that the durometer hardness will fall within the scope of the present invention. Such modifications may be determined by routine testing.

A coating according to a second embodiment of the present invention comprises a mixture of polyurethane and polyurea and is made from mixing a urethane prepolymer with an amine component. It may also comprise further additives such as the ones previously mentioned.

The urethane prepolymer is prepared by reacting an isocyanate with a polyol as described in relation with the first embodiment. The hydroxy groups of the polyol will thus react with the isocyanate groups of the diisocyanate to form a urethane prepolymer. However, unlike the first

embodiment in which the coating comprises only polyurethane and additives, if any, the molar ratio of the polyol to the isocyanate is determined so that the urethane prepolymer will have isocyanate terminal groups, hence the use of the expression "prepolymer". Preferably, the ratio of polyol to isocyanate is chosen so that there will be between 6% to 10% excess diisocyanate in the urethane prepolymer.

The isocyanate terminal groups of the urethane prepolymer are then mixed with an amine component to form a coating composition comprising a mixture of polyurethane and polyurea.

The amine component is preferably a diamine. Suitable diamines include α,ω-alkylenediamine having preferably between 2 to 6 carbon atoms and aromatic diamines such as 4,4'-methylene bis(2-chloroaniline), 2,4-toluene diamine,diethyl or 4,4'-methylene dianiline.

While it is possible to mix the urethane prepolymer directly with the amine component, it is however preferable, for handling purposes, if the amine component is mixed with a suitable glycol that acts as a chain extender. Thus, the amine component may be a diamine mixed with an α,ω-glycol having between 2 and 6 carbon atoms or mixtures thereof. Most preferably, the mixture is obtained by mixing equal amounts of 4,4'-methylene dianiline with an approximately 75:25 mixture of two α-hydro-ω-hydroxypoly [oxy(methyl-1,2-ethanediyls)] having a molecular weight of about 1000 and about 500, respectively.

The person skilled in the art will realize that it may be possible to use other amine components or mixtures provided that the stoichiometric ratio is adjusted to take into consideration the variations in molecular weight. Examples of other suitable amine components include 4,4'-methylene bis(2-

chloroaniline) or 2,4-toluene diamine,diethyl. Similarly, other glycols, such as α-hydro-ω-hydroxypoly (oxy-1,4-butanediyl) could be used.

Additives, such as the ones described in relation with the first embodiment may also be used.

The invention will be further understood by the description of the following example that constitutes a preferred embodiment of the invention and that should not be construed in a limiting manner:

Example 1

COMPOSITION

Ingredient	**% by weight**
Mixture A (urethane prepolymer)	
MONDUR TD-80 [1]	~30
TERATHANE 1000 and 2000 [2]	~60
mixture B (amine component and additives)	
4,4'-methylene dianiline	~5
α-hydro-ω-hydroxypoly [oxy(methyl-1,2-ethanediyl)] [3]	~5
carbon black	~0.25

[1] approximately 80:20 mixture of toluene-2,4-diisocyanate and toluene-2,6-diisocyanate.
[2] approximately 90:10 mixture of two α-hydro-ω-hydroxypoly (oxy-1,4-butanediyls) having molecular weights of about 1000 and about 2000, respectively.
[3] approximately 75:25 mixture of two α-hydro-ω-hydroxypoly [oxy(methyl-1,2-ethanediyls)] having molecular weights of about 1000 and about 500, respectively.

The ingredients of mixture A were mixed together in a first chamber and were heated to a temperature of about 70°C±10°C. Similarly, the ingredients of mixture B, including any other additives, were mixed together in a second chamber and were also heated to a temperature of about 70°C±10°C.

Mixtures A and B were then mixed together in a 2:1 ratio (two part mixture A and one part mixture B) and the resulting composition was applied to a wood hockey stick blade by using a spray gun. A PROBLER gun (Product of Glas-Craft) with a 17:1 fluid to air ratio was found to be suitable for this. The use of such a spray gun facilitates the coating operation since the two mixtures A and B are only mixed at the tip of the gun thereby preventing premature solidification of the composition. In a variant, the tip of the spray gun may be removed and the composition may be applied as a bead. The person skilled in the art will however realize that the composition may be applied to the blade using other similar equipment or other coating techniques known in the art. A preferred thickness for roller hockey is approximately from 10 to 50 mils and preferably from 20 to 30 mils but the thickness may vary according to the intended use. Also, the coating may be applied in a single application or in a series of applications. In the latter case however, each coating is not left to dry before the other coating is applied.

The composition was then left to dry under normal conditions and solidified thereby providing an abrasion resistant coating. A period of between 40 to 60 seconds was found to be sufficient to complete the drying.

PHYSICAL PROPERTIES

The coating of example 1 exhibited the following properties:

Property	Result	Test
Hardness (durometer Shore D)	50D±5D [1]	ASTM D-2240
Tensile strength (psi)	3200	ASTM D-412
Elongation (%)	300	ASTM D-412
Resiliency (%)	45	ASTM D-2632

[1] This value is equivalent to a durometer hardness of at least 90A.

The coating of example 1 was tested on pavement and on an ice rink and provided satisfactory results.

While the coating of the second embodiment was prepared by a urethane prepolymer with an amine component, in yet a third embodiment, the coating could be prepared by mixing a diisocyanate with a mixture comprising a polyol, an amine component and additives, if any. For apparent reasons, a less dangerous diisocyanate such as diphenylmethane diisocyanate should preferably be used in such an embodiment instead toluene-2,4-diisocyanate and toluene-2,6-diisocyanate.

Because of the relatively fast solidification time of the composition, the use of the coating of the present invention may improve the efficiency of the manufacturing process of hockey stick blade thereby lowering costs. Furthermore, the use of the coating according to the invention avoid the use of volatile organic compounds which might be released into the atmosphere and is thus safer for the environment.

The above description of a preferred embodiment should not be interpreted in any limiting manner since variations and refinements are possible which are within the spirit and scope of the present invention. The scope of the invention is defined in the appended claims and their equivalents.

THE EMBODIMENTS OF THE INVENTION FOR WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A hockey stick blade having a lower edge for contacting a surface of play, at least a portion of said lower edge bearing an abrasion resistant coating comprising polyurethane, said coating having a durometer hardness of at least about 70A.

2. A blade as defined in claim 1 wherein said coating comprises polyurethane and polyurea.

3. A blade as defined in claim 2 wherein said coating is made by mixing a urethane prepolymer having isocyanate terminal groups with an amine component.

4. A blade as defined in claim 3 wherein said urethane prepolymer is made by reacting a mixture of toluene-2,4-diisocyanate and toluene-2,6-diisocyanate with an α,ω-glycol having between 2 and 6 carbon atoms, mixtures thereof or a low molecular weight polymer thereof and wherein said amine component is a diamine which is mixed with an α,ω-glycol having between 2 and 6 carbon atoms or mixtures thereof.

5. A blade as defined in claim 4 wherein said urethane prepolymer is made by reacting a mixture of toluene-2,4-diisocyanate and toluene-2,6-diisocyanate with an α-hydro-ω-hydroxypoly (oxy-1,4-butanediyl) and wherein said amine component is a mixture of 4,4'-methylene dianiline with an α-hydro-ω-hydroxypoly [oxy(methyl-1,2-ethanediyl)].

6. A hockey stick blade having a lower edge for contacting a surface of play, at least a portion of said lower edge bearing an abrasion resistant coating having a durometer hardness of at least about 70A, said coating being

made by mixing a urethane prepolymer with an amine component, said urethane prepolymer being made by reacting an approximately 80:20 mixture of toluene-2,4-diisocyanate and toluene-2,6-diisocyanate with an approximately 90:10 mixture of two α-hydro-ω-hydroxypoly (oxy-1,4-butanediyls) having molecular weights of about 1000 and about 2000, respectively, said amine component being a mixture of 4,4'-methylene dianiline with an approximately 75:25 mixture of two α-hydro-ω-hydroxypoly [oxy(methyl-1,2-ethanediyls)] having molecular weights of about 1000 and about 500, respectively.

7. A blade as defined in claim 1 wherein said coating is made by mixing a diisocyanate with an amine mixture comprising an amine component, an α,ω-glycol having between 2 and 6 carbon atoms, mixtures thereof or a low molecular weight polymer thereof.

8. A blade as defined in claim 7 wherein said diisocyanate is diphenylmethane diisocyanate and wherein said amine mixture comprises an α-hydro-ω-hydroxypoly (oxy-1,4-butanediyl), 4,4'-methylene dianiline and an α-hydro-ω-hydroxypoly [oxy(methyl-1,2-ethanediyl)].

9. A blade as defined in claim 1 wherein said coating is between 20 to 30 mils thick.

10. A blade as defined in claims 1, 2, 3, 4, 5, 6, and 7, wherein said coating has a durometer hardness between about 70A and about 75D.

11. A hockey stick comprising a blade coated in accordance with any claim 1.

12. A process for coating a hockey stick blade, said process comprising the step of applying to a blade a coating comprising polyurethane

and having a durometer hardness of at least 70A, said process being carried out in the absence of or substantially in the absence of solvent.

13. A process for coating a hockey stick blade, said process comprising the steps of:

a) reacting a mixture of toluene-2,4-diisocyanate and toluene-2,6-diisocyanate with an α,ω-glycol having between 2 and 6 carbon atoms, mixtures thereof or a low molecular weight polymer thereof to form a urethane prepolymer;

b) mixing a diamine with an α,ω-glycol having between 2 and 6 carbon atoms or mixtures thereof to provide an amine component;

c) mixing said urethane prepolymer and said amine component to form a coating composition; and

d) applying said composition to said blade.

14. A process as defined in claim 13 wherein said urethane prepolymer and said amine component are heated to a temperature of about 70° C ± 10° C before being admixed and applied to said blade.

15. A process as defined in claim 14 wherein the urethane prepolymer of step a) is made by reacting a mixture of toluene-2,4-diisocyanate and toluene-2,6-diisocyanate with an α-hydro-ω-hydroxypoly (oxy-1,4-butanediyl) and wherein the amine component of step b) is a mixture of 4,4'-methylene dianiline with an α-hydro-ω-hydroxypoly [oxy(methyl-1,2-ethanediyl)].

16. A process as defined in claims 13 or 14, said process being carried out in the absence of or substantially in the absence of solvent.

INTERNATIONAL SEARCH REPORT

Inter. onal Application No
PCT/CA 97/00419

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 A63B59/14 C08G18/10 C08G18/32 C08G18/48 C08G18/76
C08G18/66

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 A63B C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 332 212 A (SUSI MICHAEL F ET AL) 26 July 1994 see claims 1,2,7 see column 2, line 25 - column 3, line 16 ---	1
X	FR 2 487 208 A (BONIFACE JACQUES) 29 January 1982 see claims 1,3 see page 2, line 9 - line 22 ---	1
X	WO 96 02385 A (FULLER H B LICENSING FINANC) 1 February 1996 see claims 1-5 see page 1, line 26 - page 2, line 31 --- -/--	1,2

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
10 October 1997	24. 10. 97

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Van Puymbroeck, M

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Inte .onal Application No
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	EP 0 164 523 A (AMERICAN CYANAMID CO) 18 December 1985 see claims 1-6	1
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